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S1. Additional $^{27}$Al NMR data for Al–Cl model compounds.

Figure SI 1: A. $^{27}$Al single pulse excitation MAS spectra for a. NaAlCl$_4$, b. AlCl$_3$ and c. AlCl$_3$·6H$_2$O, spinning sidebands are marked with asterisks, note that the spinning speed for AlCl$_3$ was lower (18 kHz) than for the other compounds (35 kHz), $B_0 = 20.0$ T. B. $^{27}$Al—$^{35}$Cl TRAPDOR curves ($\Delta S/S_0$) for AlCl$_3$ (red triangles), AlCl$_3$·6H$_2$O (black stars) and NaAlCl$_4$ (blue squares), MAS speed = 35 kHz.

S2. Additional solid state NMR data for binary adducts.

Single pulse aluminium experiments are performed using standard Agilent 1.6 mm rotors. There are alternatives available in the form of ‘Al-background free’ rotors. However, these rotors are not completely Al-background free either, although they have a significantly reduced background signal. The mechanical stability of these rotors is limited, however. For example spinning speeds in a 1.6 mm MAS setup should be limited to ~ 25 kHz using these rotors. Figure SI 2 shows the intensity of the ZNCs compared to the background signal of the rotor.

Figure SI 2: $^{27}$Al single pulse 35 kHz MAS spectrum of MC-B (black), empty rotor (red) and difference spectrum (blue) at $B_0 = 20$ T.
Figure SI 3: (A., C.) $^{27}$Al and (B., D.) $^1$H MAS NMR spectra of MC-M (A., B.) and MC-B (C., D.) adducts at fields of 14.1 T (green) and 20 T (black); MAS speed = 30 and 35 kHz, respectively.
Proton 2D-exchange and double quantum-single quantum (DQSQ) experiments were performed to probe the $^1$H–$^1$H interactions. The resulting 2D spectra are displayed in Figure SI 4A-B, and two off-diagonal correlations are observed in both spectra. The exchange spectrum shows cross-peaks for the $\delta$ 0.85-1.26 ppm pair (hydrocarbon, intramolecular) and $\delta$ 2.3-7.2 ppm pair. It should be noted that the mixing time is very long and hence the interaction between both pairs is very weak, something which is probably related to the mobility of these species as is indicated by their narrow lines as well. When the contour levels are drawn at much lower levels some other very weak correlations show up between the hydrocarbon (0.85/1.26 ppm) signals and the 2.3/7.2 ppm signals as well as correlations to a broad signal at 3.90 ppm, which probably indicates that all these components are adsorbed on the surface.

A DQSQ spectrum shows slightly different information compared to an exchange spectrum. The 2:1 ‘diagonal’ only shows signal if the protons involved have protons of the same type in their direct vicinity. This will, for example, always be the case for protons in a CH$_2$- or CH$_3$-group. CH-groups do not automatically show up in a DQSQ spectrum. However, a diagonal peak for such a group can still be observed when equivalent CH-groups are in close proximity to each other. The absence of a ‘diagonal’ peak for a resonance that is observed in a regular 1D therefore points to a chemical group with a single proton that is isolated enough to not communicate with a group of the same type. ‘Cross peaks’ between a pair of resonances, A and B, show up at ($\delta_a$, $\delta_{a+b}$) and ($\delta_b$, $\delta_{a+b}$) and can even be found for resonances without a diagonal peak.

The cross peaks for the $\delta$ 0.85-1.26 ppm pair and the $\delta$ 2.3-7.2 ppm pair are also found in the DQSQ spectrum, and they are again weak. The cross peak is stronger for 7.21 compared to 7.30 ppm. It is interesting to see a connectivity between the signals at 2.3 and 7.2 ppm as they are the two peaks that have increased in intensity after the disappearance of the Al-CH$_3$ signal. To test whether these resonance could result from coordination to a metal or halide, TRAPDOR correlation experiments are performed. From $^1$H–{$^{27}$Al} and $^1$H–{$^{35}$Cl} TRAPDOR experiments, see Figure SI 5, it follows that these resonances are not linked to aluminium or chlorine. In the absence of signal indicating an Al-alkyl, the $^1$H–{$^{27}$Al} TRAPDOR shows hardly any effect. The broader signals between 3-5 ppm show some intensity loss. A $^1$H–{$^{35}$Cl} TRAPDOR experiment was also performed and it only shows a $^1$H–{$^{35}$Cl} interaction for the Mg-OH surface group at 1.68 ppm. Note
that faster spinning, as in the $^1$H–$^{35}$Cl TRAPDOR experiment, leads to some narrowing of the broad signals between 3-5 ppm explaining the apparent difference between the spectra in Figure SI 5A-B.

The two new resonances have quite a remarkable shift; δ 7.2-7.3 ppm generally belongs to aromatic protons or alternatively to N-H protons, while δ 2.3 ppm can belong to an benzylic methyl group. Based on the chemical shifts and the observed connectivities, it would appear that these signals belong to toluene. Relative intensities of the peaks are also in agreement with this assignment where 7.21 ppm refers to the ortho- and para-hydrogens and 7.30 to the meta position, which also explains the different interaction strength in the DQSQ experiment. As mentioned before, the signals are also detected in the initial sample. However, it is unknown where the toluene comes from as it is not used in the synthesis. Also, there is no obvious explanation as to why it shows up so much more prominent after the loss of the Al-alkyl group; apparently the mobility increased. Note that the signals can also be found in the ternary adducts.

Figure SI 5: $^1$H–$^{27}$Al and B. $^1$H–$^{35}$Cl TRAPDOR experiment for the degraded MC-M at $B_0 = 20.0$ T. Total TRAPDOR dephasing time is 16 ms in A. and 17 ms in B., while the MAS speed is 12.5 and 35 kHz respectively, $\nu_{RF}^{27}$Al = 120 kHz and $\nu_{RF}^{35}$Cl = 30 kHz.
S3. Additional solid state NMR data for ternary systems.

![Graph showing 
$^{27}$Al–$^{35}$Cl TRAPDOR and 
$^{35}$Cl–$^{27}$Al TRAPDOR spectra for TMC-M.](image)

Figure SI 6: A. $^{27}$Al–$^{35}$Cl TRAPDOR and B. $^{35}$Cl–$^{27}$Al TRAPDOR spectra for TMC-M with the reference in black and the TRAPDOR spectrum with 17 ms irradiation in blue.

We conducted $^{27}$Al–$^{35}$Cl TRAPDOR experiments for ternary adducts TMC-M and TMC-B. This might be informative about which aluminium sites have the strongest interaction with chlorine, which could be very informative for spectral assignment. Surface chlorines are not detected directly and $^{35}$Cl–$^{27}$Al TRAPDOR are therefore unlikely to show interactions. It takes much longer to acquire a decent $^{27}$Al or $^{35}$Cl spectrum compared to $^1$H. Because of time constraints we therefore investigated the potential TRAPDOR effect only at some longer irradiation times instead of acquiring whole TRAPDOR curves. The results for TMC-M can be seen in Figure SI 6. The S/N-ratio for these spectra is rather poor, but it seems that both TRAPDOR experiments failed to show any $^{27}$Al–$^{35}$Cl interaction, both for TMC-M and TMC-B (not shown). Given the weak TRAPDOR effects that were found for the Al–Cl reference compounds, where aluminium is surrounded by 4-6 chlorine at short distances, it might not come as a surprise that TRAPDOR did not work for the cocatalyst samples, in particular because of the much worse spectral quality of the spectra.

S4. EPR data for ternary systems.

![Graph showing Room temperature X-band EPR spectrum for TMC-B and TMC-M.](image)

Figure SI 7: Room temperature X-band EPR spectrum for TMC-B (top) and TMC-M (bottom).

S5. Additional solid state NMR data for donor containing systems.
Figure SI 8: $^{13}$C MAS spectra for a. binary, b. ternary and c. quaternary system containing the DMFluo donor at 9.4 T using 75 kHz $^1$H decoupling and MAS speeds of 15-18 kHz.

Figure SI 9: $^{13}$C MAS spectrum of Do2-M at various temperatures at 9.4 T showing the spectra before (bottom) and after (top) a cooling cycle. The bottom spectrum was acquired using 50 kHz $^1$H decoupling, while 75 kHz $^1$H decoupling was used for the other spectra.

The MC-D samples were further investigated using carbon NMR at fields of 20.0 and 9.4 T, with low temperature measurements at the lower field. The $^{13}$C spectra, acquired at 15 or 18 kHz MAS, for the different adducts (Do2-M, Do2-M & Do2-MD) are compared to each other in Figure SI 8, and illustrate the absence of DMDMS. They show peaks at 54, 65, 81, 120-129, 140 and 145 ppm that can be assigned to the carbons of the DMFluo donor. The 20 T data show spinning sidebands at 213 and 45 ppm. The latter is overlapping with other peaks in the aliphatic region that do not belong to the DMFluo donor. There are peaks at 15, 23, 33 and 42 ppm that were previously assigned to hydrocarbons (pentane/heptane) which are
used during synthesis. However, the consistency of the peak intensities in the various samples would argue against residual solvent peaks. Moreover, it cannot explain the peak at 42 ppm. Also, there is additional signal in the $^1$H spectra.

Conformational freedom can impose problems for calculating chemical shifts as many structures need to be considered. We choose DMFluo as a rigid molecule and decided to perform low temperature measurements to freeze out potential mobility that could still be present at room temperature. VT measurements were performed for Do2_2.5 and Do2-M at temperatures down to 133 K. The series of $^{13}$C CPMAS spectra is shown in Figure SI 9, for Do2-M. Hardly any changes in the spectra is observed, suggesting that mobility at room temperature is already strongly restricted for this donor. DMFluo should therefore be a good donor to compare calculated vs experimentally observed chemical shifts.

![Figure SI 10: A. $^{35}$Cl MAS and B. $^{13}$C CP MAS spectra for Do2-MD at 20.0 T measured before exposure (red) and after a long exposure of the sample (black). The 'before' signal in the $^{35}$Cl spectrum is displayed at 28 % of its original intensity, the blue line shows the difference between the black and red curve and the dotted line is a simulation.](image-url)